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1 **Indoor secondary pollutants from household product emissions in the**

2 **presence of ozone. A bench-scale chamber study**

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11 **Abstract**

12   Ozone-driven chemistry is a major source of indoor secondary pollutants of health

13 concern. This study investigates secondary air pollutants formed from reactions between

14 constituents of household products and ozone. Gas-phase product emissions were introduced

15 along with ozone at constant rates into a 198-L Teflon-lined reaction chamber. Gas-phase

16 concentrations of reactive terpenoids and oxidation products were measured. Formaldehyde was

17 a predominant oxidation byproduct for the three studied products, with yields under most

18 conditions of 20-30% with respect to ozone consumed. Acetaldehyde, acetone, glycolaldehyde,

19 formic acid and acetic acid were each also detected for two or three of the products. Immediately

20 upon mixing of reactants, a scanning mobility particle sizer detected particle nucleation events

21 that were followed by a significant degree of ultrafine particle growth. The production of

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1   secondary gaseous pollutants and particles depended primarily on the ozone level and was

2   influenced by other parameters such as the air-exchange rate. Hydroxyl radical concentrations in

3   the range $0.04\text{-}200 \times 10^5$ molecules cm^{-3} were measured. OH concentrations were observed to

4   vary strongly with residual ozone level in the chamber, which was in the range 1 – 25 ppb, as is

5   consistent with expectations from a simplified kinetic model. In a separate test, we exposed the

6   dry residue of two products to ozone in the chamber and observed the formation of gas-phase

7   and particle-phase secondary oxidation products.

8   **Introduction**

9   The use of cleaning products and air fresheners indoors can cause inhalation exposure of

10 cleaning personnel and building occupants to toxic air contaminants (TACs) (*1, 2*). In addition

11 to direct emission of toxic constituents, many products contain terpenoids that can react rapidly

12 with ozone yielding secondary pollutants, including secondary organic particulate matter (*3*).

13 Ozone is commonly present indoors owing to intrusion from outdoor air. Indoor sources of

14 ozone also exist, including some office equipment and certain "air purifiers" that can generate

15 indoor ozone levels of hundreds of ppb (*4, 5*). The products of ozone reactions with terpenoids

16 include volatile carbonyls, some of which are TACs (e.g., formaldehyde and acetaldehyde).

17 Ozone-terpenoid reactions also produce the hydroxyl radical. Due to their high reactivity, these

18 species can generate additional TACs different from those directly produced by terpene-ozone

19 reaction and increase the yields of certain products such as formaldehyde and aerosol particles

20 (*6*).

21   Little is known about the indoor concentrations of TACs as secondary pollutants from

22 cleaning products and air fresheners. Such concentrations depend on the complex interplay of

23 many factors and processes, including product composition, usage, emission dynamics, transport

1   and mixing, building ventilation, sorptive interactions with building surfaces and reactive

2   chemistry. The goal of this study is to provide experimental information on the rate and extent of

3   formation of secondary pollutants from terpenoid-containing household products in the presence

4   of ozone. Bench-scale chamber experiments permit control of key variables such as reagent

5   concentrations, mixing ratios, air-exchange rate, temperature and relative humidity.

6   **Experimental methods**

7   *Reaction chamber and ancillary apparatus*

8   The reaction of ozone with cleaning product/air freshener components was studied in a

9   198-L stainless-steel flow reaction chamber, internally lined with FEP-Teflon film. The chamber

10   was operated under positive pressure and was provided with two inlet ports on opposite corners

11   and an outlet port. A constant flow of air and the product gas-phase components was introduced

12   into one port, and an air stream containing ozone was admitted at the other inlet. Chamber

13   temperature and RH were measured and continuously recorded. The experimental apparatus was

14   housed in a 20-m^3 environmental room at $23.0 \pm 0.5\ ^\circ$C. The main airflow to the chamber, of

15   compressed "zero quality" air, was split between a dry and a humidified stream and adjusted

16   using mass flow controllers to obtain an RH between 40 and 60%. Well-mixed conditions within

17   the chamber were demonstrated with SF_6, which was introduced at either inlet and continuously

18   monitored at the outlet using an infrared analyzer. The all-Teflon reactor minimized the surface

19   interactions of the studied chemicals, including ozone decomposition on surface materials.

20   Ozone was generated by means of UV irradiation of an airstream flowing at 100 mL/min.

21   Immediately before and after each run, the ozone inlet concentration was measured directly

22   employing a calibrated ozone monitor, to determine the amount of O_3 introduced in the chamber

23   and to verify its stability. Otherwise, the ozone monitor continuously sampled from the chamber

1   outlet and the data were logged at 1-min intervals. In preliminary runs, we verified that inlet

2   concentrations accurately represented ozone chamber concentrations in the absence of VOCs.

3   Flows of background air, product components and ozone were measured before and after the

4   experiments with a precision better than 2 %.

5   *Characterization and delivery of household products emissions*

6   Three common US retail products containing ozone-reactive chemicals were employed: a

7   general-purpose pine oil-based cleaner (POC), an orange oil-based degreaser containing d-

8   limonene as the sole active ingredient (OOD), and a plug-in scented-oil air freshener (AFR).

9   Gas-phase components of the first two products were delivered to the reaction chamber from an

10   80-L Tedlar bag prepared by adding a measured amount of the product and air, heating in an

11   incubator at 50 °C for 2 h, and then cooling to room temperature. A peristaltic pump delivered a

12   constant flow (in the range 20-100 mL/min) into the main airflow. For the air freshener, an 80-L

13   stainless steel drum replaced the Tedlar bag. Inside the drum, the product was continuously

14   electrically powered, as in ordinary use, and a stream of air flowing at 100 mL/min introduced

15   the volatile components into the main air stream. Experiments were designed to closely replicate

16   VOC concentrations determined during realistic use of the products in a 50-m^3 chamber (*7*).

17   Composition of the gas-phase emissions from the selected products was determined in

18   previous work (*7*). The three main volatile ingredients of POC were d-limonene, terpinolene and

19   α-terpineol. Other monoterpenes were detected in smaller quantities (α- and γ-terpinene, α- and

20   β-pinene, camphene, γ-terpineol and α-phellandrene), together with additional VOCs (p-cymene,

21   eucalyptol). Organic emissions from the OOD were exclusively d-limonene. By contrast, more

22   than 30 volatile components were detected from the AFR, including d-limonene and a variety of

23   alcohols (linalool, dihydromyrcenol, β-citronellol) and esters (linalyl acetate, bornyl acetate).

1   *Sampling and analytical methods*

2   VOCs were sampled onto Tenax®-TA sorbent tubes connected in parallel immediately

3   after the outlet port. Two adjacent sampling ports were used to collect samples on DNPH-coated

4   silica cartridges preceded by an ozone scrubber to determine volatile carbonyls and on NaOH-

5   coated silica cartridges to determine volatile carboxylic acids. Ozone scrubbing was determined

6   to be unnecessary for the VOC by collecting simultaneous samples of different volumes.

7   VOCs collected in Tenax sorbent tubes were analyzed by thermal desorption-gas

8   chromatography-mass spectrometry (TD/GC/MS) using an HP6890 GC equipped with a

9   Chrompack TCT 4020 desorber with cryogenic trap and interfaced to an HP5973 mass selective

10   detector (MSD) that operated in electron impact mode. Details of the GC-MSD method are given

11   elsewhere (*8*). DNPH-coated cartridges were extracted with 2 mL acetonitrile. DNPH-carbonyl

12   derivatives present in the extracts were analyzed at 360 nm by HPLC provided with a UV

13   detector. NaOH-coated silica cartridges were extracted with deionized water, and the extracts

14   were analyzed by ion chromatography.

15   *Experimental procedure*

16   We investigated the effect of two parameters on each of the three products: reaction time

17   using air exchange (ach) rates of 1 ach and 3 ach, and the ozone level using 120-130 (high) and

18   60 ppb (moderate) inlet concentrations. The effect of low (30 ppb) and very high (250 ppb) inlet

19   O_3 levels were   also investigated with the POC product. VOC concentrations in the reaction

20   chamber were determined at the beginning of each experiment before ozone was added, during

21   the first 2-4 h. Subsequently, ozone was introduced at a constant flow rate and VOC

22   concentrations were again measured once steady state was achieved. Reactant consumption and

23   product yields were calculated by difference.

1   *Determination of OH radical concentration*

2   For determination of OH radical concentrations, we adopted a method employed by

3   Weschler and Shields (*9*). A stream of 1,3,5-trimethylbenzene (TMB) and perchloroethylene

4   (PCE) was generated with diffusion tubes placed in a thermostat at 40 $^{\circ}$C and supplied at a

5   constant rate to the reaction chamber. The TMB/PCE ratio was used to estimate the

6   concentration of OH radical in the system, assuming that TMB reacted significantly with OH but

7   negligibly with O_3 at our short residence times; PCE served as an inert tracer. Both chemicals

8   were sampled on Tenax sorbent tubes in the absence and presence of ozone, and analyzed by

9   TD/GC/MS.

10   *Particle sampling*

11   Particle size distributions of sampled chamber air were measured with a scanning

12   mobility particle sizer (SMPS) system that utilized a differential mobility analyzer (3071A, TSI

13   Inc.) coupled with a condensation particle counter (3760, TSI Inc.). The system was configured

14   to measure particle sizes from 8 to 412 nm. Size distributions were obtained at 1-min intervals

15   using software developed by Donald Collins (Texas A&M University) and Patrick Chuang

16   (UCSC). For selected experiments, an optical particle counter (OPC, Lasair 1003) extended the

17   particle size range up to 2 μm. Aerosol particle sampling was performed continuously, starting

18   before the introduction of ozone.

19   *Surface application*

20   Separately, the reactions of ozone with semivolatile or nonvolatile components of the

21   POC and the OOD were evaluated through the application of a 0.5-mL aliquot to a 0.09 m^2 glass

22   plate. After removing the excess liquid, the plate was placed in a 10-L stainless steel cell and

23   exposed for 1.5 h to a N_2 flow at an air-exchange rate of 3 ach to remove the more volatile

1   components. At the end of the volatilization period, only α- and γ-terpineol were still evidently

2   being emitted by the surface from the POC application, and no VOCs were detected for the

3   OOD. The plate was then placed in the 198-L reaction chamber, which had been previously

4   conditioned at 120 ppb O_3 and operated at an air-exchange rate of 1 ach. The plates were exposed

5   to ozone under the same conditions for 24 hours. Chamber ozone and aerosol concentrations

6   were monitored continuously starting before the introduction of the plate. VOC and carbonyl

7   samples were collected periodically.

8   **Results and Discussion**

9   In Figures 1-2 and Tables 1S-3S we present data obtained from experiments with the

10   three household products in the presence of various levels of ozone in supply air and at low and

11   high residence times (air-exchange rates of 3 ach and 1 ach, respectively). In the tables, the

12   values shown in the concentration (C) column are ozone in the absence of reactive VOCs and

13   VOCs before addition of ozone. Oxidation product concentrations are those measured at steady

14   state in the presence of ozone. For oxidation products that were present before ozone was added

15   (acetone and acetic acid), the value reported in Tables 1S-3S represents the increase due to

16   reaction, i.e., the difference between those measured with and without ozone. The second data

17   column indicates the fractions of ozone and VOCs that reacted and the yield of oxidation

18   products. Percent yield is the ratio of oxidation product generated (ppb) to ozone consumed

19   (ppb) during the reaction. Ozone consumption was calculated as the difference between inlet and

20   residual ozone levels. Figures 1 and 2 illustrate the VOC consumption and oxidation product

21   yields for each condition. In Figures 2-A and 2-C, total yields higher than 100% indicate that

22   some products may have originated at more than one step in the oxidation sequence or that OH

1   radicals generated in terpene-ozone reactions are involved in the production of additional

2   oxidation products.

3   For the seven VOC components from the POC shown in Table 1S, only one — α-

4   terpinene — reacted substantially and unambiguously under all test conditions. Four compounds

5   — d-limonene, terpinolene, and α- and γ-terpineol — reacted substantially in some test

6   conditions. Eucalyptol and p-cymene were relatively inert, as expected based on their

7   bimolecular rate constants with ozone. The results for α-terpineol for the high ozone and high

8   air-exchange condition suggest reactivity towards ozone that is similar to that of d-limonene, in

9   agreement with a recent determination (*10*). Its isomer, γ-terpineol, reacted at faster rates, similar

10   to those of terpinolene. The α-terpineol results are not consistent between the two high ozone

11   experiments. The reproducibility of α-terpineol concentrations among samples collected in the

12   same steady-state period also was low. These observations might be related to sorption of α-

13   terpineol on chamber surfaces. The vapor pressures of the major constituents of the POC are

14   relatively high (between 0.6 and 5 torr), while that of α-terpineol is roughly two orders of

15   magnitude lower (0.023 torr) (*11*). In the high ozone experiments about 90% of the α-terpinene

16   was consumed, compared with roughly 30-40% of the terpinolene and 15-20% of the d-

17   limonene. For these three species, the apparent relative reactivity was roughly proportional to the

18   product of their concentration and their reported reaction rates with ozone: 2×10^{-14}, 2×10^{-15}

19   and 2×10^{-16} cm^3 molecule^{-1} s^{-1}, respectively (*12*). Ozone was substantially titrated by the excess

20   of reactive VOCs in all experiments, so that the steady-state ozone level in the chamber was no

21   greater than 10% of that in the supply air. Consistent with expectations, the table reveals that

22   across all five ozone levels the observed extent of reaction depended more on the residual ozone

23   level, which varied from < 1 ppb to ~ 25 ppb, than on the characteristic reaction time, which only

1   varied from 0.3 to 1.0 h. The fraction of α-terpinene, terpinolene and d-limonene consumed in

2   each condition is shown in Figure 1-A.

3   In Figure 1-B and Table 2S, we present data from exposing the emissions of OOD to

4   ozone. Owing to the large excess in d-limonene, and although this chemical readily reacts fully

5   to the extent possible based on the amount of ozone present, ~ 20% of this species reacted under

6   high ozone and 10% under low ozone conditions, while consuming more than 80% of the

7   chamber ozone at 3 ach, and almost completely depleting it (95%) at 1 ach.

8   The formulation of AFR was the most complex among the studied products, with more

9   than 30 components. A higher extent of sorption can be attributed to the fact that vapor pressures

10   of alcohols and esters in AFR were significantly lower than those of hydrocarbons from POC

11   and OOD. Only five AFR components exhibited significant reactivity toward ozone under these

12   experimental conditions, including linalool and d-limonene, the two most reactive ingredients.

13   The concentration of linalool was about twice as high as that of d-limonene. Two different

14   reports have placed the reaction rate of linalool with ozone at values that are similar to or slightly

15   higher than that of d-limonene: at $k < 3.16 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} and $k = 4.3 \times 10^{-16}$ cm^3

16   molecule^{-1} s^{-1} (*12*). Their reaction rates with OH radicals are comparable, $k = 1.69 \times 10^{-10}$ cm^3

17   molecule^{-1} s^{-1} for d-limonene and k $= 1.59 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for linalool (*12*). We

18   observed that linalool was more completely consumed, except for the moderate ozone condition

19   in which d-limonene showed similar reactivity. Other reactive species in the air freshener were

20   dihydromyrcenol, linalyl acetate and β-citronellol. While data on the bimolecular reaction rate of

21   these terpenoids with ozone have not been published, our results suggest that the reaction rate of

22   β-citronellol is comparable to that of linalool, the rate of linalyl acetate compares to that of d-

1   limonene and dihydromyrcenol reacts at a slower rate. Experimental data are shown in Table 3S

2   and plotted in Figure 1-C.

3   *Volatile oxidation products*

4   Formaldehyde yields were similar for the reaction of POC and OOD with ozone (in the

5   range 20-30% for most conditions) and higher for AFR (30-90%). The fact that several distinct

6   terpene-based products led to high formaldehyde yields in the presence of ozone is an important

7   result of this study, since formaldehyde is a toxic air contaminant with a low chronic reference

8   exposure level (*13*). Although formaldehyde can be generated at various steps of oxidation of

9   most reactive VOCs (not only by ozonation but also through reaction with OH radicals and other

10   oxidant species) its principal chemical source in our system is the ozonation of d-limonene and,

11   when present, linalool. Formaldehyde is produced as a primary carbonyl during ozonation of the

12   terminal alkene group in d-limonene with a yield of $\phi_F = 0.10$-0.19 (*14*). The contribution of that

13   reaction to total formaldehyde production ($X_{primary}$) can be estimated for the OOD data shown in

14   Table 2S, assuming that d-limonene is the single reactant and formaldehyde is the only carbonyl

15   detected:

16
$$X_{primary} = \frac{\phi_F [O_3]_{consumed}}{[F]_{produced}} \tag{1}$$

17   Considering a lower limit for the formaldehyde yield of $\phi_F = 0.10$, the fraction of formaldehyde

18   generated as a primary carbonyl in the ozonation of d-limonene from the OOD is $X_{primary} = 0.33$

19   for high O_3 and 3 ach, 0.40 for high O_3 and 1 ach, and 0.45 for moderate O_3 and 3 ach. Higher

20   yields of formaldehyde measured in AFR experiments are probably due to the presence of two

21   reactive VOCs that generate formaldehyde as the primary carbonyl during ozonation (d-

22   limonene and linalool). Similarly, the high acetone concentration measured for POC and AFR

1   likely originated in the primary ozonation of terpinolene and linalool, respectively. Background

2   levels of oxidation products before ozone addition were negligible except for acetone, present at

3   5ppb in POC.

4   Oxidation product yields reported for AFR in Table 3S show a significant increase for

5   experiments at 1 ach (up to 90 % for formaldehyde), suggesting an important effect owing to the

6   longer residence time that was not observed with POC and OOD. Low vapor pressures can be

7   expected for several AFR components that exhibited GC retention times higher than those of

8   POC components. Likely, such species can sorb to surfaces and react there with ozone in the

9   chamber, thus contributing to the measured gas-phase concentration of oxidation products. While

10   sorption of semivolatile components may be viewed as a limitation of the chamber method

11   employed here, these results are of interest considering that similar processes would likely occur

12   on indoor surfaces, possibly leading to analogous production of volatile oxidation products.

13   Considering the two volatile carboxylic acids detected, formic acid is an oxidation

14   product of formaldehyde and is present at 30-80% of the formaldehyde level. Acetic acid is

15   generated either in tertiary oxidation reactions or by hydrolysis of esters. In particular,

16   background levels (i.e., without ozone) of acetic acid were high for AFR (160-170 ppb),

17   presumably due to partial hydrolysis of major fragrance components such as borneol acetate,

18   linalyl acetate or phenylethyl acetate.

19   Glycolaldehyde is a biogenic VOC commonly measured together with terpenes and their

20   oxidation products in environmental samples. Spaulding et al. (*15*) identified glycolaldehyde

21   among other oxygenated airborne chemicals collected at a pine plantation. Glycolaldehyde in our

22   study is likely generated in the reaction of OH with partially oxidized terpenes. High yields of

23   glycolaldehyde have been measured in the reaction of OH with biogenic VOCs such as 2-

1   methyl-3-buten-2-ol, MBO, (~60%), allyl alcohol (47%), 1-penten-3-ol (87%) and Z-2-penten-1-

2   ol (90%) (*16-18*). We did not obtain a positive identification for benzaldehyde, methylglyoxal or

3   acrolein, but cannot rule out the presence of acrolein owing to sampling limitations.

4   *OH radical concentrations*

5   We determined the concentration of OH radicals in the system through measuring its

6   reaction with 1,3,5-trimethylbenzene. Figure 3 shows the OH concentrations measured at each

7   condition for the three products as a function of the residual O_3 concentration in the chamber.

8   These results are consistent in magnitude with those of Weschler and Shields (*9*) employing d-

9   limonene and ozone mixtures, as well as with direct OH determinations in ozone/alkene mixtures

10 using a laser-induced fluorescence method (*19*). The OH radical is short-lived, so that its

11 concentration effectively depends on the dynamic balance between the rate of production and the

12 rate of consumption by chemical reactions. Those rates depend on concentrations of residual

13 ozone and reactive VOCs. The pseudo-steady state balance can be approximated as:

14
$$[OH] = \frac{\sum_i k_i y_i [O_3][U_i]}{\sum_i h_i[U_i] + \sum_j h_j[S_j]} \qquad (2)$$

15 where k_i is the bimolecular reaction rate between ozone and the unsaturated chemical U_i; y_i is the

16 corresponding OH formation yield; h_i and h_j are the bimolecular reaction rates for OH with

17 unsaturated (U_i) and saturated (S_j) VOCs, respectively. High OH yields, between 0.38 and 0.74,

18 have been reported for several of the studied terpenes (*20*). Typical k_i values are in the range 10^{-17}-10^{-14} cm^3 molecule^{-1} s^{-1}, while h_i is in the range of 5×10^{-10} to 5×10^{-11} cm^3 molecule^{-1} s^{-1} and h_j

20 is in the range of 5×10^{-11} to 5×10^{-12} cm^3 molecule^{-1} s^{-1} (*12*). Equation 2 does not explicitly

1   consider possible reactions of OH with secondary products from ozone-terpene reactions, which

2   result in additional sinks for OH.

3   For cases in which the terpenoids are the most significant OH sinks (i.e., $\Sigma h_i[U_i] \gg$

4    $\Sigma h_j[S_j]$), the steady-state OH radical concentration can be estimated in terms of only the

5   concentration of ozone and the unsaturated VOCs (U_i), as follows:

6
$$[OH] = [O_3]\left(\frac{\sum_i k_i y_i [U_i]}{\sum_i h_i [U_i]}\right)$$
(3)

7   The dominance of terpenoids as OH sinks appears to be a good approximation for our

8   experiments with POC and OOD, but is less accurate for AFR, which contains substantial

9   quantities of saturated species in addition to the terpenoids. In the case of OOD, which contains

10   only one reactive unsaturated VOC (d-limonene), the approximate equation can be further

11   simplified to be independent of the concentration of d-limonene:

12
$$[OH] = [O_3]\frac{k_i y_i}{h_i}$$
(4)

13   Figure 3 includes traces that correspond to the simplified models expressed by equations 3 and 4.

14   The magnitude and trend agreement between these approximation and the experimentally

15   determined OH level indicates that the simple models capture the key features of OH radical

16   chemistry in these experiments, particularly at the higher air-exchange rate. Model overestimates

17   for the lower air-exchange rates may be a consequence of the relatively higher concentrations of

18   secondary oxidation products that would constitute an important additional sink for OH radicals.

1   *Secondary organic aerosol formation*

2   Figure 4 shows the temporal evolution of airborne particle number concentration (A),

3   volume concentration (B) and size distribution (C) for particles in the size range 8 - 412 nm

4   measured with the SMPS in one experiment where AFR volatile components were exposed to

5   moderate ozone levels (63 ppb inlet concentration). Total number and volume concentration

6   were calculated by integration from the size distribution, and therefore do not account for

7   particles that have grown out of the measurement range of the SMPS. Qualitatively similar

8   behavior was observed for all household products and experimental conditions. The most

9   distinctive feature in all cases was the burst of ultrafine particle nucleation that occurred

10   immediately upon ozone addition (indicated with an arrow in frame C). Qualitatively, these

11   results are consistent with recent reports of ultrafine particle formation and growth during the

12   reaction of ozone with terpenes ([21-23]). Remarkably, the production of ultrafine aerosol particles

13   observed here is similar in its main features to nucleation events observed in the atmosphere ([24,

14   25]) although the mixing ratio of terpenoids to ozone is significantly higher in our experimental

15   conditions where ozone is virtually titrated by the large excess of the reactive alkene.

16   The total particle number concentrations, together with their corresponding aerosol mass

17   (assuming density = 1 g/cm^3) are reported in Table 4S. We report values for the ultrafine fraction

18   (< 0.1 µm diameter, PM $_{0.1}$), for the total particles measured with the SMPS (PM $_{0.4}$) and, when

19   available, for total particles measured with the optical counter (PM $_{2.0}$). Data were calculated at

20   both peak conditions (~ 20 – 40 minutes after initial introduction of O_3 to the system) and at

21   steady-state conditions (> 2 h or > 4 h after the start of O_3 addition for 3 ach and 1 ach,

22   respectively). Initial particle growth rates in the range 2 – 6 nm min^{-1} are also reported in Table

23   4S. The large number of particles measured at the peak of the burst was predominantly in the

1   ultrafine fraction (diameter < 0.1 µm), although larger particles accounted for $70-80$ % of the

2   peak particle mass under most experimental conditions. Peak particle concentrations scaled in

3   proportion to the ozone and VOC consumed. When the amount of ozone and VOC that reacted at

4   each experimental condition was similar for the three household products, the amount of $PM_{0.1}$

5   produced at the peak was largest for POC, followed by OOD and AFR. Such differences can be

6   rationalized by considering the combined product of the initial concentrations of the reactive

7   VOCs (U_0) and their reaction rate with ozone (k_{O3}), $\sum_i U_0 k_{O3}$, which varied in the same order

8   (POC > OOD > AFR). In addition, characteristics of the reaction byproducts are expected to

9   affect the nucleation process. For example, the four reactive VOCs in the POC and the single

10   reactive terpene in OOD (d-limonene) each have at least one endocyclic unsaturation that yields

11   C_{10} primary oxidation products upon ozonation. Conversely, of the four most reactive

12   constituents in AFR, three react with ozone to fragment their carbon backbone, yielding products

13   with 9 or fewer carbon atoms, and therefore less likely to nucleate or condense. Experiments run

14   at 1 ach showed lower peak particle production than at 3 ach for POC and OOD. However, for

15   AFR, the trend was reversed.

16   At steady state, the ultrafine particle concentrations were markedly lower than the peak

17   values, representing 30-70 % of the total number concentration and only 1-4 % of the total mass

18   concentration for most experimental conditions. Following nucleation, aerosol aging processes

19   led to particle growth from the ultrafine to the accumulation mode (0.1-2 µm diameter) as shown

20   in Figure 4. An estimation of aerosol particle yield (mass/mass) can be obtained from the ratio

21   of the steady-state $PM_{2.0}$ mass concentration (when available) to the sum of reacted VOCs

22   concentration in each product. We so determined yields of 6-14 % for POC components, 11-16%

23   for OOD (using $PM_{0.4}$ values) and 4-6 % for AFR. Yields determined for POC and OOD are

1   similar to those reported for ozone/d-limonene reactions (*26, 27*). The relatively lower values for

2   AFR are consistent with reported observations for reactions of linalool with ozone (*27*).

3   *Surface application*

4   A dry residue was obtained by applying a small quantity of the POC or the OOD to a

5   glass plate, allowing it to dry under a flow of nitrogen to remove the volatile components. During

6   subsequent exposure of the dry POC residue to ozone in the reaction chamber, initially high

7   concentrations of α- and γ-terpineol (~ 1 ppm and 100 ppb, respectively) were measured at 15

8   and 100 min after introducing the plate. A measurement at 200 minutes showed declining values

9   for the concentrations of the two terpenoids (350 and 15 ppb respectively). During the first 3 h of

10   ozone exposure, we observed the production of formaldehyde (with an average concentration

11   during that period of 4.6 ppb), acetaldehyde (0.9 ppb), acetone (9.9 ppb) and glycolaldehyde (1.5

12   ppb). Figure 5 shows the evolution of the ozone concentration in the chamber during the

13   experiment (Fig 5-C) together with the measurement of aerosol particle number (Fig 5-A),

14   volume (Fig 5-B) and particle size distribution (Fig 5-D). We observed a burst of ultrafine

15   particle formation during the initial exposure of reagents that was similar to those measured in

16   gas-phase experiments. The time evolution of the particle volume concentration mirrors closely

17   the ozone curve shown in Fig 5-C. Owing to the combined ozone exposure of the terpenoid

18   reactants in both the gas phase and on the surface, we cannot discern the degree to which the

19   observations are a result of homogeneous versus heterogeneous chemistry. However, when the

20   same experiment was performed with dry residue from OOD, no primary VOCs were detected in

21   the gas phase during the exposure to ozone but we did observe the formation of oxidation

22   products during the initial 4 h of exposure (3.3 ppb formaldehyde, 2.8 ppb acetaldehyde and 11

23   ppb acetone). A burst of ultrafine particles and secondary aerosol growth similar to that shown in

Figure 5 for POC was also observed when OOD dry residue was exposed to ozone. These tests suggest that delayed desorption of reactive terpenoids of low volatility or the reaction of nonvolatile chemicals on the surface may constitute a source of secondary oxidation products and secondary organic aerosol.

Significance

This laboratory investigation illustrates the potential impact of ozone-initiated chemistry involving constituents of common household products and leading to the formation of secondary gaseous pollutants and particles. Widespread use of cleaning products and air fresheners in close proximity to humans suggests that the reactive chemistry presented here may contribute significantly to indoor exposure to certain toxic air contaminants and to ultrafine secondary organic aerosol. Key findings include:

- Confirmation that terpenoids present in household products react with ozone to produce high yields of formaldehyde (up to 90 %) and other TACs.

- High hydroxyl radical concentrations at levels that can generate other TACs.

- The same reactions contribute to the formation of ultrafine particles with yields of 4-16%.

- Ozone was the limiting reagent at levels 1-25 ppb; thus, in locations of high outdoor ozone levels similar product use may lead to even higher exposures to TACs and aerosols.

- Formaldehyde and aerosols were produced from the exposure of product dry residue to ozone, indicating that surface reactions can be an additional significant source of indoor pollutants.

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13

1   **Figure Captions**

2

3   **Figure 1**   Consumption of reactive VOCs from (A) pine-oil based cleaner; (B) orange oil-based degreaser

4   and (C) plug-in air freshener. Error bars indicate S.D. (n=2). Ozone consumption for the same

5   experiments was 82-100 %, being the limiting factor that prevented further VOC loss.

6   **Figure 2**   Yield of oxidation products relative to ozone consumption (mole/mole) for (A) pine-oil based

7   cleaner; (B) orange oil-based degreaser and (C) plug-in air freshener.

8   **Figure 3**   Hydroxyl radical concentration versus residual ozone concentration for experiments with (A)

9   pine-oil based cleaner, (B) orange oil-based degreaser, and (C) plug-in air freshener. Solid

10   traces correspond to simplified models expressed by equations 3 and 4. Error bars indicate S.D.

11   (n=2).

12   **Figure 4**   SMPS measurements of secondary organic aerosol particles generated in the reaction of plug-in

13   air freshener VOCs with ozone at moderate levels (63 ppb in supply air) and 3 ach: (A) particle

14   number concentration; (B) particle volume concentration; (C) particle size distribution in the

15   range 8-412 nm. Dp is the particle aerodynamic diameter. Numbers indicated in boxes

16   correspond to the particle number concentration (# cm^{-3}) for each contour line.

17   **Figure 5**   SMPS measurements of secondary organic aerosol particles generated when a plate containing

18   dry residue of a pine oil-based cleaner was introduced in the chamber operating at high ozone

19   levels (120 ppb in supply air) and at 1 ach: (A) particle number concentration; (B) particle

20   volume concentration; (C) ozone chamber concentration; (D) particle size distribution in the

21   range 8-412 nm. Dp is the particle aerodynamic diameter. Numbers indicated in boxes

22   correspond to the particle number concentration (# cm^{-3}) for each contour line.

TABLE 1S. Reaction of Ozone with Pine Oil-Based Cleaner Components

species	very high O$_3$; 3 ach C (ppb)	very high O$_3$; 3 ach reacted (%)	high O$_3$; 3 ach C (ppb)	high O$_3$; 3 ach reacted (%)	high O$_3$; 1 ach C (ppb)	high O$_3$; 1 ach reacted (%)	moderate O$_3$; 3 ach C (ppb)	moderate O$_3$; 3 ach reacted (%)	low O$_3$; 3 ach C (ppb)	low O$_3$; 3 ach reacted (%)
ozone [a]	253 ± 4	90 ± 10	131 ± 4	90 ± 7	130 ± 13	94 ± 15	65 ± 2	97 ± 11	29 ± 1	100 ± 58
VOC components [b]										
α-terpinene	22.5 ± 1	96 ± 2	25 ± 1	92 ± 3	25 ± 2	89 ± 4	24 ± 2	72 ± 7	16 ± 1	67 ± 2
d-limonene	204 ± 6	25 ± 2	219 ± 2	17 ± 0.7	229 ± 6	15 ± 2	206 ± 5	1.2 ± 3.8	202 ± 3	4 ± 1
p-cymene	40 ± 2	-3 ± 3	41 ± 0.5	1.2 ± 1.3	42 ± 2	1.6 ± 3.1	37 ± 2	-4.4 ± 5.2	49 ± 1	0 ± 2
eucalyptol	53 ± 2	-3 ± 2	58 ± 0.4	3.3 ± 0.5	60 ± 2	2.6 ± 2.5	46 ± 9	-19 ± 13	53 ± 1	-2 ± 2
terpinolene	240 ± 8	66 ± 4	266 ± 12	43 ± 3	266 ± 14	33 ± 4	236 ± 32	8 ± 12	130 ± 3	12 ± 2
α-terpineol	146 ± 3	23 ± 2	149 ± 4	14 ± 2	104 ± 3	-9 ± 2	154 ± 25	-2 ± 11	104 ± 18	-18 ± 13
γ-terpineol	18 ± 2	66 ± 5	13 ± 2	41 ± 8	12 ± 1	19 ± 3	19 ± 3	16 ± 12	11 ± 2	-4 ± 14
volatile oxidation products [c]										
	C (ppb)	yield (%)	C (ppb)	yield (%)	C (ppb)	yield (%)	C (ppb)	yield (%)	C (ppb)	yield (%)
formaldehyde	59 ± 1	26 ± 1	34.5 ± 1	28 ± 1	35 ± 0.5	27 ± 0.4	13 ± 0.5	20 ± 1	4.6 ± 0.6	16 ± 2
acetaldehyde	4.4 ± 0.8	1.9 ± 0.3	2.2 ± 2.3	1.0 ± 1.3	2.2 ± 1.2	1.0 ± 0.5	1.6 ± 1.1	0.8 ± 0.6	nd [d]	
acetone	123 ± 3	54 ± 1	81 ± 5	66 ± 4	83 ± 3	63 ± 2	29 ± 1	45 ± 2	7.5 ± 4.7	26 ± 16
glycolaldehyde	17 ± 2	7.4 ± 0.7	11 ± 0.3	4.9 ± 0.1	12 ± 0.4	5.2 ± 0.2	5.4 ± 0.3	2.6 ± 0.1	3.5 ± 0.1	12 ± 1
formic acid	40 ± 9	17 ± 4	26.5 ± 4	22 ± 4	12 ± 5	9 ± 4	10 ± 15	15 ± 23	4 ± 15	13 ± 26
acetic acid	55 ± 9	24 ± 4	38 ± 7	31 ± 6	22 ± 12	17 ± 9	3 ± 22	5 ± 33	nd [d]	

Concentrations (C) are reported for these conditions: [a] ozone level in reaction chamber without cleaning products; [b] VOC components in reaction chamber without ozone; and [c] volatile oxidation products in reaction chamber with both ozone and VOC components. [d] nd = not detected.
Errors correspond to ±S.D. of duplicate determinations

1

TABLE 2S. Reaction of Ozone with Orange Oil-Based Degreaser Components

3

species	high O₃; 3 ach		high O₃; 1 ach		moderate O₃; 3 ach	
	C (ppb)	reacted (%)	C (ppb)	reacted (%)	C (ppb)	reacted (%)
ozone [a]	137 ± 9	85 ± 6	136 ± 7	95 ± 17	61 ± 2	82 ± 12
VOC components [b]						
d-limonene	643 ± 20	19 ± 2	738 ± 14	20 ± 6	586 ± 4	9.9 ± 1.1
volatile oxidation products [c]						
	C (ppb)	yield (%)	C (ppb)	yield (%)	C (ppb)	yield (%)
formaldehyde	32 ± 0.3	28 ± 0.2	36 ± 1	28 ± 1	13 ± 0.5	26 ± 1
formic acid	14 ± 5	12 ± 4	19 ± 12	15 ± 9	4 ± 7	7 ± 15
acetic acid	20 ± 10	17 ± 8	31 ± 22	24 ± 18	8 ± 40	16 ± 81

4 Concentrations (C) are reported for these conditions: [a] ozone level in reaction chamber without cleaning products; [b] VOC
5 components in reaction chamber without ozone; and [c] volatile oxidation products in reaction chamber with both ozone and
6 VOC components.
7 Errors correspond to ±S.D. of duplicate determinations

8
9

TABLE 3S. Reaction of Ozone with Air Freshener Components

species	high O_3; 3 ach		high O_3; 1 ach		moderate O_3; 3 ach	
	C (ppb)	reacted (%)	C (ppb)	reacted (%)	C (ppb)	reacted (%)
ozone [a]	126 ± 6	86 ± 15	127 ± 5	97 ± 67	63 ± 0.5	89 ± 11
VOC components [b]						
d-limonene	121 ± 2	29 ± 2	165 ± 11	29 ± 7	108 ± 3	22 ± 3
linalool	176 ± 3	36 ± 2	247 ± 17	41 ± 6	170 ± 4	20 ± 3
linalyl acetate	66 ± 7	22 ± 9	88 ± 8	25 ± 12	57 ± 3	19 ± 24
dihydromyrcenol	241 ± 3	4.5 ± 1.4	335 ± 23	6 ± 11	242 ± 6	7 ± 3
β-citronellol	19 ± 1	40 ± 2	24 ± 2	40 ± 7	19 ± 1	25 ± 5
volatile oxidation products [c]						
	C (ppb)	yield (%)	C (ppb)	yield (%)	C (ppb)	yield (%)
formaldehyde	41 ± 0.4	38 ± 0.4	111 ± 2	90 ± 1	16 ± 2	29 ± 4
acetaldehyde	nd [d]		13 ± 0.4	11 ± 0.4	nd [d]	
acetone	41 ± 5	38 ±52	95 ± 1	77 ± 1	14 ± 0.6	25 ± 1
glycolaldehyde	13 ± 0.3	12 ± 0.2	33 ± 0.5	27 ± 0.4	7 ± 0.3	13 ± 0.5
formic acid	24 ± 6	22 ± 6	68	55	14 ± 6	25 ± 11
acetic acid	36 ± 23	34 ± 22	84	68	nd [d]	

Concentrations (C) are reported for these conditions: [a] ozone level in reaction chamber without cleaning products; [b] VOC components in reaction chamber without ozone; and [c] volatile oxidation products in reaction chamber with both ozone and VOC components. [d] nd = not detected.
Errors correspond to ±S.D. of duplicate determinations

TABLE 4S. Secondary Organic Aerosol Formation

| Condition | Initial Growth rate (nm min⁻¹) | peak concentrations | | | | steady-state concentrations | | | | |
		number (10^5 cm⁻³) $PM_{0.1}$ $PM_{0.4}$ $PM_{2.0}$	mass [a] (µg m⁻³) $PM_{0.1}$	$PM_{0.4}$	$PM_{2.0}$	number (10^5 cm⁻³) $PM_{0.1}$	$PM_{0.4}$ $PM_{2.0}$	mass [a] (µg m⁻³) $PM_{0.1}$	$PM_{0.4}$	$PM_{2.0}$
pine oil-based cleaner (POC)										
very high O₃, 3 ach	4.5	3.6	72	306	306	0.06	0.16	1.0	107	215
high O₃, 3 ach	3.8	2.4	46	162	162	0.04	0.11	0.7	67	115
high O₃, 1 ach	1.6	1.6	27	102	n.a.	0.05	0.14	1.0	68	n.a.
moderate O₃, 3 ach	2.6	1.2	19	57	n.a.	0.13	0.24	1.4	50	n.a.
Low O₃, 3 ach	2.6	0.5	8	12	12	0.07	0.1	1.0	11	11
orange-oil based degreaser (OOD)										
high O₃, 3 ach	5.8	1.4	37	229	n.a.	0.06	0.18	1.2	105	n.a.
high O₃, 1 ach	3.6	0.8	18	192	n.a.	0.03	0.13	0.7	90	n.a.
moderate O₃, 3 ach	5.0	0.6	15	75	n.a.	0.05	0.13	1.0	53	n.a.
air freshener (AFR)										
high O₃, 3 ach	5.0	0.4	10	51	51	0.04	0.08	0.7	33	45
High O₃, 1 ach	2.3	0.9	20	90	90	0.02	0.05	0.3	37	65
moderate O₃, 3 ach	4.3	0.2	6	21	21	0.04	0.07	0.6	15	15

[a] Mass concentration of particles assuming density of 1.0 g cm⁻³.
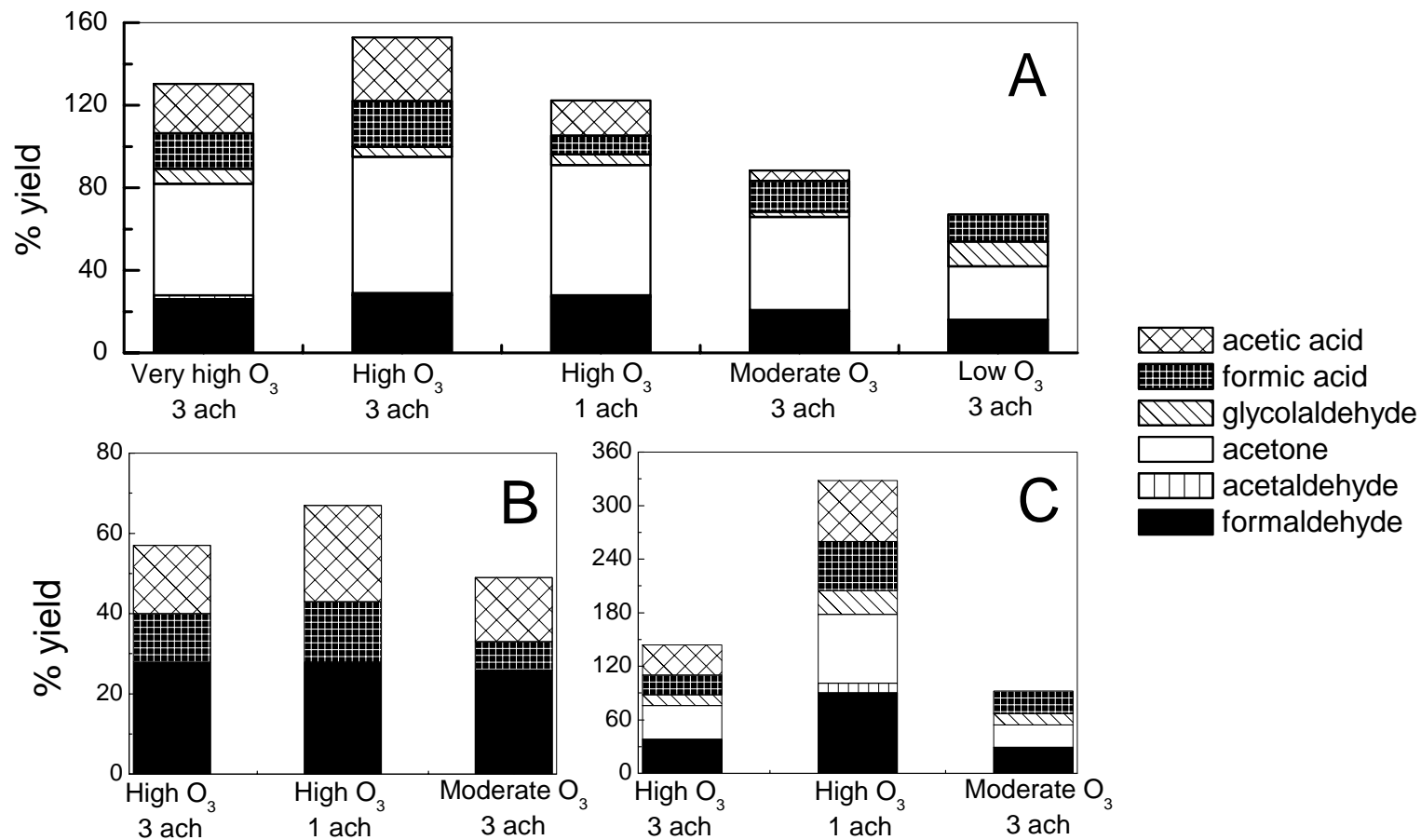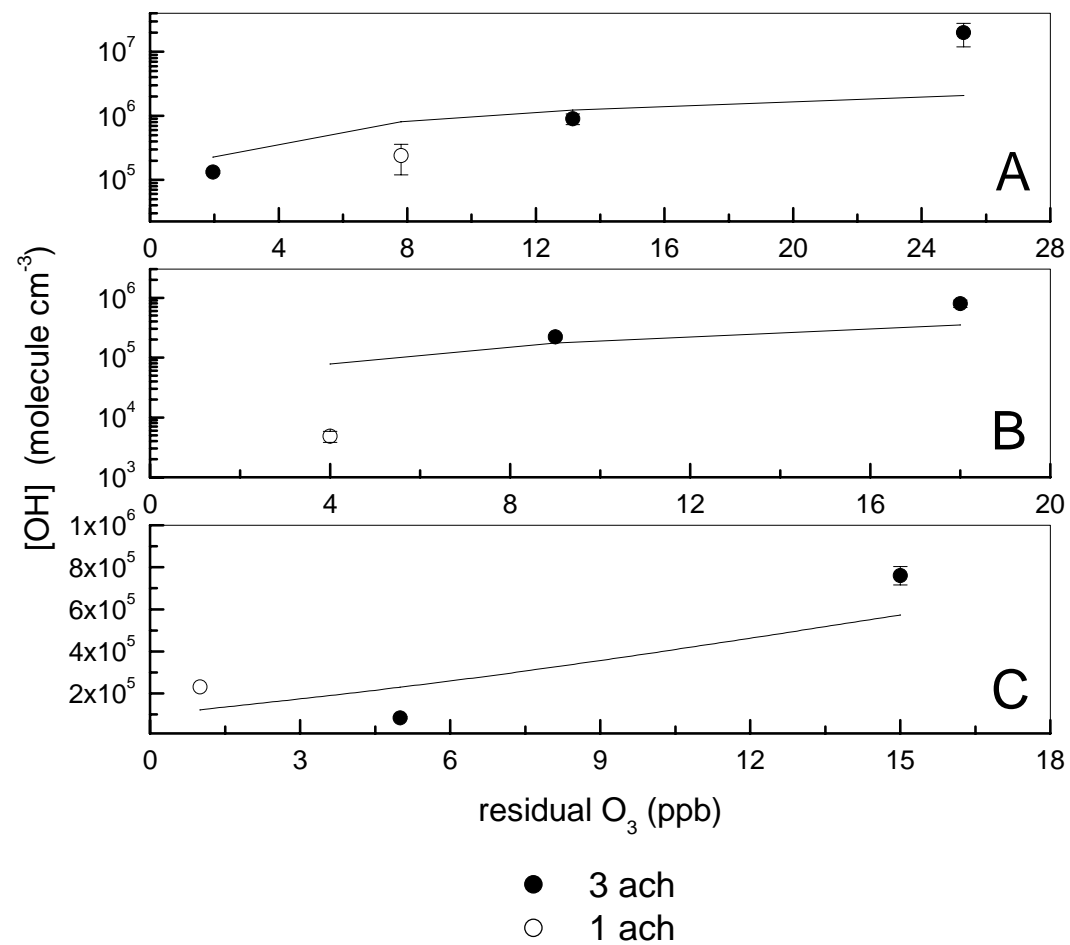n.a.: data not available
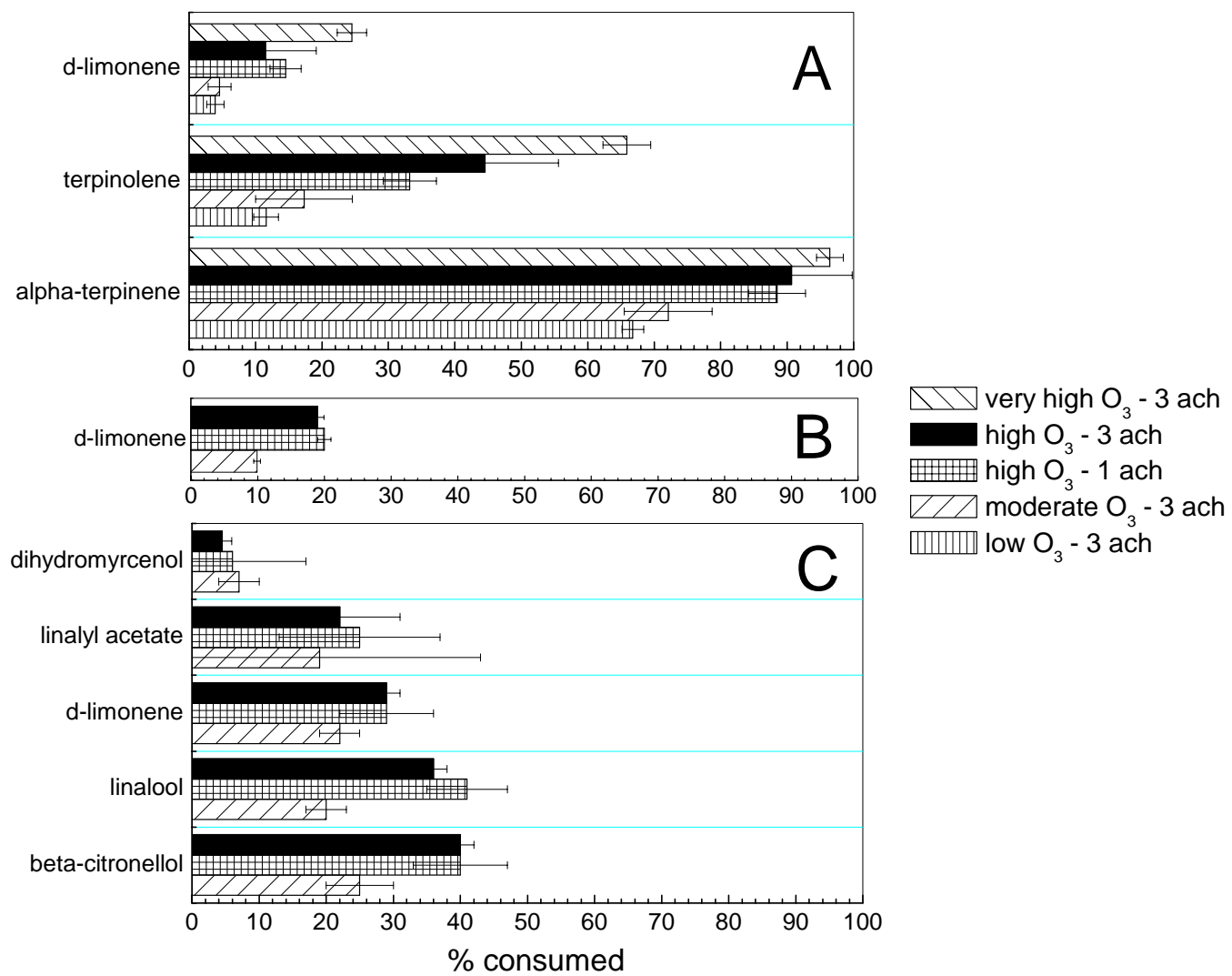
FIGURE 1

FIGURE 2
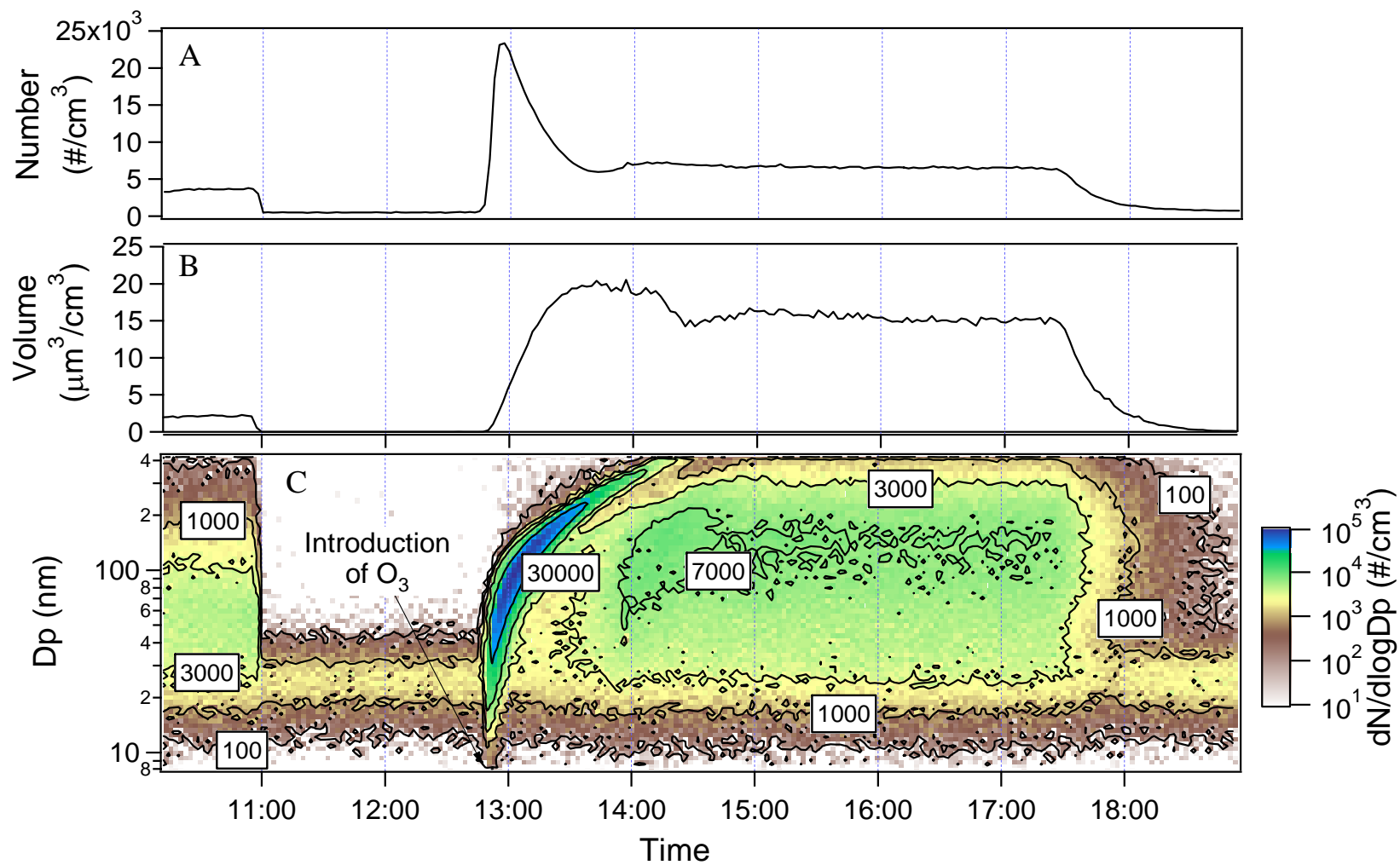
FIGURE 3

FIGURE 4

FIGURE 5